

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

Public Reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimates or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188,) Washington, DC 20503.

| | | |
|---|-------------------------------|--|
| 1. AGENCY USE ONLY (Leave Blank) | 2. REPORT DATE May 19 2001 | 3. REPORT TYPE AND DATES COVERED Final. 6/01/96 to 10/31/01 |
| 4. TITLE AND SUBTITLE Molecular Structure for smart materials. | | 5. FUNDING NUMBERS DAAH049610231-005 |
| 6. AUTHOR(S) J. Spence | | |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Arizona State University, Physics. | | 8. PERFORMING ORGANIZATION REPORT NUMBER |
| 9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211 | | 10. SPONSORING / MONITORING AGENCY REPORT NUMBER |
| 11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation. | | |
| 12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited. | | 12 b. DISTRIBUTION CODE |

| | | | | | |
|--|-----------------------------|--|--|---|--|
| REPORT DOCUMENTATION PAGE | | | Form Approved OMB No. 0704-0188 | | |
| Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS. | | | | | |
| 1. REPORT DATE (DD-MM-YYYY) 19-05-2001 | | 2. REPORT TYPE | | 3. DATES COVERED (FROM - TO) 01-06-1996 to 31-10-2001 | |
| 4. TITLE AND SUBTITLE Molecular Structure for smart materials Unclassified | | | 5a. CONTRACT NUMBER | | |
| | | | 5b. GRANT NUMBER | | |
| | | | 5c. PROGRAM ELEMENT NUMBER | | |
| 6. AUTHOR(S) | | | 5d. PROJECT NUMBER | | |
| | | | 5e. TASK NUMBER | | |
| | | | 5f. WORK UNIT NUMBER | | |
| 7. PERFORMING ORGANIZATION NAME AND ADDRESS Arizona State Univ. Physics Dept. Tucson, AZ00000 | | | 8. PERFORMING ORGANIZATION REPORT NUMBER | | |
| 9. SPONSORING/MONITORING AGENCY NAME AND ADDRESS , | | | 10. SPONSOR/MONITOR'S ACRONYM(S) | | |
| | | | 11. SPONSOR/MONITOR'S REPORT NUMBER(S) | | |
| 12. DISTRIBUTION/AVAILABILITY STATEMENT APUBLIC RELEASE , | | | | | |
| 13. SUPPLEMENTARY NOTES | | | | | |
| 14. ABSTRACT This project has developed new electron diffraction methods for determining the structure of organic sensors and detectors, including a colorimetric diacetylene phospholipid which changes color when exposed to toxins, and a new hard covalent carbonate. We are concerned with radiation-sensitive molecules which cannot be crystallized for analysis by X-ray crystallography, and with new nanostructured organics which do not form large enough single crystals for X-ray analysis. Since the main problem is radiation damage, we have studied this problem in detail. The use of low electron energies to reduce radiation damage has proven effective. We have obtained the first transmission electron diffraction patterns at a beam energy below the carbon K -shell ionization energy (285 eV). We have designed and constructed a field-emission point-projection electron microscope (PPM), a facility for making coated nanotip field emitters, a low energy electron diffraction camera, and facilities for making thin organic films by the Langmuir Blodgett and other methods. The PPM has successfully given nanometer-resolution coherent electron holograms and reconstructed images, at 200 eV, of Tobacco Mosaic Virus. In addition, we have solved a new organic crystal structure whose sub-micron grain-size prevented it being solved by any other method. This material holds promise as a hard, light, optical material. In summary, we now have the hardware and software in place to image useful organic molecules which do not form large enough crystals for conventional analysis. | | | | | |
| 15. SUBJECT TERMS | | | | | |
| 16. SECURITY CLASSIFICATION OF: | | 17. LIMITATION OF ABSTRACT Public Release | 18. NUMBER OF PAGES 6 | 19. NAME OF RESPONSIBLE PERSON Cornell, Elizabeth ecornell@dtic.mil | |
| a. REPORT Unclassified | b. ABSTRACT Unclassified | c. THIS PAGE Unclassified | | 19b. TELEPHONE NUMBER International Area Code Area Code Telephone Number - DSN - | |
| | | | | Standard Form 298 (Rev. 8-98) Prescribed by ANSI Std Z39.18 | |

13. ABSTRACT (Maximum 200 words)

This project has developed new electron diffraction methods for determining the structure of organic sensors and detectors, including a colorimetric diacetylene phospholipid which changes color when exposed to toxins, and a new hard covalent carbonate. We are concerned with radiation-sensitive molecules which cannot be crystallized for analysis by X-ray crystallography, and with new nanostructured organics which do not form large enough single crystals for X-ray analysis. Since the main problem is radiation damage, we have studied this problem in detail. The use of low electron energies to reduce radiation damage has proven effective. We have obtained the first transmission electron diffraction patterns at a beam energy below the carbon K-shell ionization energy (285 eV). We have designed and constructed a field-emission point-projection electron microscope (PPM), a facility for making coated nanotip field emitters, a low energy electron diffraction camera, and facilities for making thin organic films by the Langmuir Blodgett and other methods. The PPM has successfully given nanometer-resolution coherent electron holograms and reconstructed images, at 200 eV, of Tobacco Mosaic Virus.

In addition, we have solved a new organic crystal structure whose sub-micron grain-size prevented it being solved by any other method. This material holds promise as a hard, light, optical material. In summary, we now have the hardware and software in place to image useful organic molecules which do not form large enough crystals for conventional analysis.

| | | | |
|---|--|---|---|
| 14. SUBJECT TERMS Organic molecules, Structure determination, Sensors, Detectors, Molecular electronics, radiation damage, Bio-sensors, Smart materials. | | | 15. NUMBER OF PAGES |
| | | | 16. PRICE CODE |
| 17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED | 18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED | 19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED | 20. LIMITATION OF ABSTRACT UL |

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)
Prescribed by ANSI Std. Z39-18
298-102

GENERAL INSTRUCTIONS FOR COMPLETING SF 298

The Report Documentation Page (RDP) is used for announcing and cataloging reports. It is important that this information be consistent with the rest of the report, particularly the cover and title page. Instructions for filling in each block of the form follow. It is important to ***stay within the lines*** to meet ***optical scanning requirements***.

Block 1. Agency Use Only (Leave blank)

Block 2. Report Date. Full publication date including day, month, and year, if available (e.g. 1 Jan 88). Must cite at least year.

Block 3. Type of Report and Dates Covered.

State whether report is interim, final, etc. If applicable enter inclusive report dates (e.g. 10 Jun 87 - 30 Jun 88).

Block 4. Title and Subtitle. A title is taken from the part of the report that provides the most meaningful and complete information. When a report is prepared in more than one volume, repeat the primary title, and volume number, and include subtitle for the specific volume. On classified documents enter the title classification in parentheses.

Block 5. Funding Numbers. To include contract and grant numbers; may include program element number(s) project number(s), task number(s), and work unit number(s). Use the following labels:

| | |
|--------------------------------|--|
| C - Contract | PR - Project |
| G - Grant | TA - Task |
| PE - Program Element | WU - Work Unit Accession No. |

Block 6. Author(s). Name(s) of person(s) responsible for writing the report, performing the research, or credited with the content of the report. If editor or compiler, this should follow the name(s).

Block 7. Performing Organization Name(s) and Address(es). Self-explanatory.

Block 8. Performing Organization Report Number. Enter the unique alphanumeric report number(s) assigned by the organization performing the report.

Block 9. Sponsoring/Monitoring Agency Name(s) and Address(es) Self-explanatory.

Block 10. Sponsoring/Monitoring Agency Report Number. (if known)

Block 11. Supplementary Notes. Enter information not included elsewhere such as; prepared in cooperation with....; Trans. of...; To be published in.... When a report is revised, include a statement whether the new report supersedes or supplements the older report.

Block 12a. Distribution/Availability Statement.

Denotes public availability or limitations. Cite any availability to the public. Enter additional limitations or special markings in all capitals (e.g. NORFORN, REL, ITAR).

DOD - See DoDD 4230.25, "Distribution Statements on Technical Documents."
DOE - See authorities.
NASA - See Handbook NHB 2200.2.
NTIS - Leave blank.

Block 12b. Distribution Code.

DOD - Leave Blank
DOE - Enter DOE distribution categories from the Standard Distribution for unclassified Scientific and Technical Reports
NASA - Leave Blank.
NTIS - Leave Blank.

Block 13. Abstract. Include a brief (*Maximum 200 words*) factual summary of the most significant information contained in the report.

Block 14. Subject Terms. Keywords or phrases identifying major subject in the report.

Block 15. Number of Pages. Enter the total number of pages.

Block 16. Price Code. Enter appropriate price code (NTIS *only*).

Block 17. - 19. Security Classifications. Self-explanatory. Enter U.S. Security Regulations (i.e., UNCLASSIFIED). If form contains classified information, stamp classification on the top and bottom of the page.

Block 20. Limitation of Abstract. This block must be completed to assign a limitation to the abstract. Enter either UL (Unlimited) or SAR (same as report). An entry in this block is necessary if the abstract is to be limited. If blank, the abstract is assumed to be unlimited.

1. Statement of problem studied.

New Organic materials are finding increasing uses as sensors and detectors with applications for ARO. Many of these bio-molecules cannot be crystallized for study by X-ray crystallography. This research aims to develop new methods of imaging organic materials at sub-nanometer resolution in order to understand and improve their function. An example is the organic molecule DC8,9PC, a diacetylene phospholipid, which changes color when exposed to certain toxins. We have solved this structure by electron diffraction. The material is also used as a high resolution photoresist for nano-lithography.

2. Summary of most important results.

A. A new type of electron microscope has been designed and constructed, which, by operating at very low energy (down to 10 eV) avoids the inner-shell ionization processes which cause most radiation damage to biomolecules. This point-projection field-emission instrument forms coherent in-line Gabor holograms of molecules at about 1nm resolution. Methods for forming the required nanotip field-emitters have successfully been developed. We have used this instrument to successfully record holograms from Tobacco-Mosaic Virus, Purple Membrane (responsible for photosynthesis) and Copper Thalocyanine, and we have reconstructed images from these holograms. New methods of solving the twin-image problem of in-line holography have also been developed. The effects of coating field-emission tips to reduce work function has been studied experimentally. Extensive theoretical work has been done on the problem of extracting structural information with least damage when imaging biomolecules (see refs. below).

B. Damage Thresholds. By measuring the time in seconds it takes Bragg spots to fade out (due to radiation damage) as a function of beam energy in the TEM, we have shown that threshold energies exist. These threshold energies correspond to the main ionization energies of the atoms in the sample. Spots take much longer to fade if the beam energy is less than these threshold energies (eg at 285 eV for the carbon K shell excitation), suggesting ways to determine molecular structure with less damage. Experimentally we have obtained the first ever transmission electron diffraction patterns at energies below the carbon K ionization energy. At very low energies, the range of elastically scattered electrons increases with decreasing energy, and we have reported transmission experiments in this range.

C. Solving organic structures by Transmission Electron Diffraction (TED). We have now solved two important crystal structures by TED. The first is the colorimetric DC8,9PC, a diacetylene phospholipid, which changes color when exposed to certain toxins. Our original aim was to solve this structure with, and without, the toxin attached, in order to understand how it binds. To do this we have used the Direct Methods numerical techniques of X-ray crystallography in order to solve the phase problem of TED. These lipids are light-element thin films of known thickness (two molecular layers thick), highly suitable for this work. The use of the elastic, imaging energy -filter on our Leo 912 Omega electron microscope was crucial to this work. The second structure solved was a new light element carbonate synthesised at ASU Chemistry, consisting of a continuously bonded covalent organic crystal. This work has been submitted for publication. **The significance of this work is that our TED method can deal with the sub-micron crystallite sizes found in many of the new nano-structured materials**, which, especially if radiation sensitive, cannot be solved by conventional methods. Our method combines NMR results with TED and Direct Methods software.

3. Listing of publications.

- 158 Radiation damage and point projection imaging of biomolecules at very low voltage. J. Spence. J.Electr.Micros. 30, p. 215 (1996) . (In Japanese) ARO DAAH04-96-1-0231.
- 167 "STEM and shadow imaging of biomolecules at 6 eV beam energy". J.C.H.Spence. Micron 28, p. 101-116. (M. J. Whelan Festschrift) 1997. .ARO
- 179 "Reflection shadow imaging of crystal surface by low-voltage point-reflection microscopy Xu Zhang , Uwe Weierstall, John C. H. Spence. Ultramic. 72, p. 67-81. 1998. ARO DAAH04-96-1-0231.
- 180 "Is molecular imaging possible ?" J. Spence. Chapter in "Topics in electron diffraction and microscopy of materials" . P.B. Hirsch Ed. (Festschrift for Prof M. J. Whelan). 1999. I.O.P. London. ISBN 075030538 ARO DAAH04-96-1-0231.

- 187 “Imaging of Tobacco Mosaic Virus at 40 volts by electron holography”. U. Weierstall and J. Spence. Proc. Int. Congr. Electr. Micros. (Cancun) 1998. ARO DAAH04-96-1-0231
- 193 “Point-projection electron imaging of TMV at 40eV electron energy”. U. Weierstall, J.C.H.Spence, M. Steve K.H. Downing. Micron 30(4) p.335-338 (1999). ARO DAAH04-96-1-0231.
- 194 “Wavefront reconstruction for in-line holograms formed by pure amplitude objects”. X. Huang, J.M. Zuo and J.C.H.Spence. Applied Surf. Sci. 148, 229-234 (1999). ARO DAAH04-96-1-0231.
- 206 “Transmission electron diffraction at 200 eV and damage-thresholds below the carbon-K edge. M.R.Stevens, Q. Chen, U. Weierstall and J.Spence. Micros and Microan. 6, p. 368 (2000) (Festschrift for A. Howie). ARO DAAH04-96-1-0231.
- 214 “Image reconstruction from TEM diffraction patterns using Feinup algorithm. Q. Chen, U. Weierstall, J. Spence. Proc. MSA. 2000. In press. ARO.
- 215 Investigation of polymerized phospholipid monolayer thin film structures by energy-filtered transmission electron diffraction. M. Stevens, M.L. Longo and J. Spence. Proc MSA. (G.W.Bailey, Ed. Springer) 2000. p. 1130. ARO.
- 211 “A modern approach to x-ray holography” . M. Howells, B. Calef, C.Jacobsen, J. Spence, and W. Yun. in Proc. X- Ray Microscopy 1999. AIP Conference Proceedings. American Institute of Physics.
- 212 “Hard X-ray Microscopy and Tomography at the ALS. W. Yun, M. Howells, J.Feng, R. Celestree, C. Chang, A.MacDowell, H. Padmore, J. Spence. Proc VIIth Int Conf on X-ray Microscopy” 1999. AIP Conference Proceedings. American Inst. of Physics. p 8-14
- 220 “Structure analysis of polymerized phospholipid bilayer by TED and Direct Methods. M. Stevens, M. Longo, D. Dorset, J.Spence. Ultramic. In press ARO DAAH049610231.
- 221 “Image reconstruction from electron and Xray diffraction patterns using iterative algorithms: experiments and simulations”. U. Weierstall, Q. Chen, J. Spence, M. Howells and R. Panepucci. Ultramic. In press 2001. ARO DAAH049610231.
- 229 “Toward a practical X-ray Fourier Transform holography at high resolution”. M.R. Howells, C. Jacobsen, S. Marchesini, S. Miller, J.Spence, U.Weierstall. Nucl Instr. Methods. (Proc XRM 2000).

Several technical and interim reports have already been submitted to ARO under this award. The PhD Thesis of Dr. M. Stevens and the MSc thesis of X. Huang will be forwarded to ARO. Reprints of papers will be forwarded shortly.

4. Listing of personnel.

1. Prof J. Spence. P.I.
2. Dr. U. Weierstall. Academic Professional, supported by ASU.
3. Dr. Q. Chen. Post Doc. Supported by this award.
4. Mr. X. Huang. Supported by this award. M. Sc in Physics obtained in 1998.
5. Dr. M. Stevens. Physics PhD student supported by this award. PhD awarded 2001.
6. Several other collaborators listed in references above at other institutions, not supported by this award.

5. Report of inventions.

None.

6. Bibliography.

See reference list above.

